A new chiral coordination polymer based on $[Fe(CN)_6]^{4-}$, Cu^{2+} cations, and (2*S*,3*S*)-1,2,3,4-tetraaminobutane: synthesis, structure, and ESR spectra

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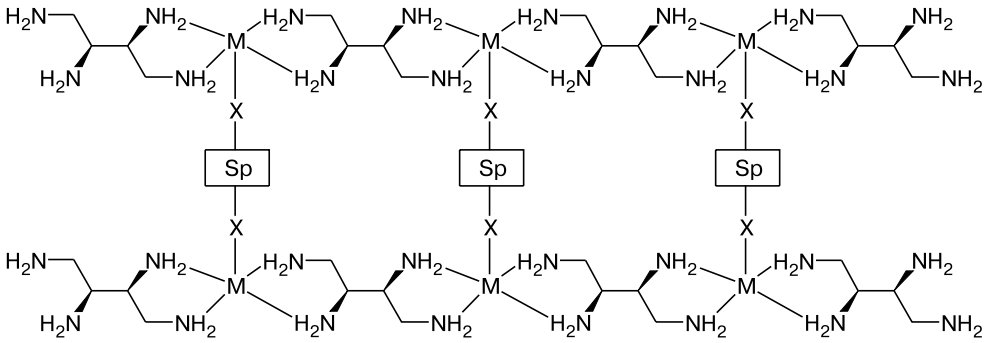
The new chiral coordination polymer $[\{Cu(NH_3)(\textit{threo}\text{-tab})\}_2Fe(CN)_6]\cdot 8H_2O$ was synthesized by the reaction of an aqueous solution of potassium hexacyanoferrate with an ammonia solution of copper(II) chloride and (2*S*,3*S*)-1,2,3,4-tetraaminobutane (*threo*-tab). The structure of the coordination polymer was established by X-ray diffraction. The ESR spectra of this compound were measured for a powder and a single crystal.

Key words: potassium hexacyanoferrate, chiral coordination polymers, polydentate amines, crystal structure.

The design of chiral structures is an important field of modern chemistry because of the diversity of their chemical and physical properties, such as enantioselective catalytic activity, specific binding of chiral guests, and electrical and optical properties.[1—5] Such chiral polymers with an open structure allow the selective binding of chiral guest molecules and, in the presence of different types of metals, make it possible to control their electronic properties. The desired chiral structures can be prepared in the synthesis of coordination polymers with the use of optically active precursors.[6—9] The choice of an appropriate pair of metals to prepare polymers with peculiar magnetic properties is another aspect of the problem.

Earlier,[10] compounds containing the chiral isomer of (2*S*,3*S*)-1,2,3,4-tetraaminobutane (*threo*-tab) with transition metal cations have been synthesized. The structure of this polyamine is such that all four N atoms cannot be simultaneously coordinated to the same metal center. The formation of oligomeric linear chains containing square-planar MN_4 fragments is a typical result of *threo*-tab co-

Scheme 1



Sp is a spacer

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Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 437—440, March, 2007.

1066-5285/07/5603-0452

ordination. An additional coordination of such metal center by spacers, which can cross-link oligomeric chains, allows the construction of porous two-dimensional chiral structures (Scheme 1).

Recently,[6,7] we have demonstrated that the chalcocyanide anions $[Re_6Q_8(CN)_6]^{4-}$ and $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, or Te) can act as cross-linking fragments in these structures. This type of compounds is characterized by the presence of extended channels, which may be of interest for catalysis and selective separation of enantiomers.

The aim of the present study was to design new compounds based on chain structures, which contain metal centers coordinated by the chiral *threo*-tab ligand. We synthesized coordination polymers with the use of mononuclear potassium hexacyanoferrate as a spacer.

Experimental

(2*S*,3*S*)-1,2,3,4-Tetraaminobutane hydrochloride *threo*-tab·4HCl was synthesized according to a procedure described earlier.[11] Other reagents are commercially available. The X- and Q-band ESR spectra were recorded on an automated Varian E-109 spectrometer at 300 and 77 K.

Synthesis of $[\{Cu(NH_3)(threo\text{-tab})\}_2Fe(CN)_6]\cdot 8H_2O$. A solution of *threo*-tab·4HCl (25 mg, 0.095 mmol) and $CuCl_2\cdot 6H_2O$ (12 mg, 0.05 mmol) in a concentrated aqueous ammonia solution (5 mL) was layered over a solution of $K_4[Fe(CN)_6]\cdot 3H_2O$ (10 mg, 0.024 mmol) in water (5 mL) and kept for ~20 °C. After two weeks, the crystals that formed were separated.

Table 1. Crystallographic data for the $[\{Cu(NH_3)(threo\text{-tab})\}_2Fe(CN)_6]\cdot 8H_2O$ complex

Parameter	Characteristic
Molecular formula	$C_{14}H_{50}Cu_2FeN_{16}O_8$
Molecular weight	753.63
Crystal dimensions/mm	0.25×0.22×0.18
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	8.8581(6)
b/Å	13.7369(9)
c/Å	13.1149(6)
β/deg	105.246(2)
V/Å^3	1539.69(16)
Z	2
d_{calc}/g cm^{-3}	1.626
μ/mm^{-1}	1.899
Ranges of reflection indices	$-12 \le h \le 9$, $-19 \le k \le 19$, $-10 \le l \le 17$
Transmission factors, min/max	0.628/0.710
Number of measured/ independent reflections	9272/7318
R_{int}	0.0262
Number of parameters in refinement	372
R ($I > 2\sigma$)	$R_1 = 0.0481$, $wR_2 = 0.1242$
R (based on all data)	$R_1 = 0.0638$, $wR_2 = 0.1314$

X-ray diffraction study. The structure of the complex was established by X-ray diffraction. The X-ray diffraction data were collected on an automated Nonius Kappa CCD diffractometer with the use of Mo-Kα radiation (0.71073 Å) and a graphite monochromator. The intensities of measured reflections were corrected for absorption using the SADABS program.[12] The crystallographic data and the structure refinement statistics are given in Table 1. The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares method using the SHELXL program package.[13,14] The H atoms were positioned geometrically and refined using a riding model with isotropic displacement parameters at the 150% level of the equivalent thermal parameters of the corresponding N atoms.

The atomic coordinates were deposited with the Cambridge Structural Database (CCDC 629259) and can be obtained from the authors.

ESR spectroscopy. The experimental ESR spectra (*1*) of a powder of this compound measured at frequencies of 9.5 and 35.5 GHz and the corresponding simulated ESR spectra (*2*) are presented in Fig. 1.

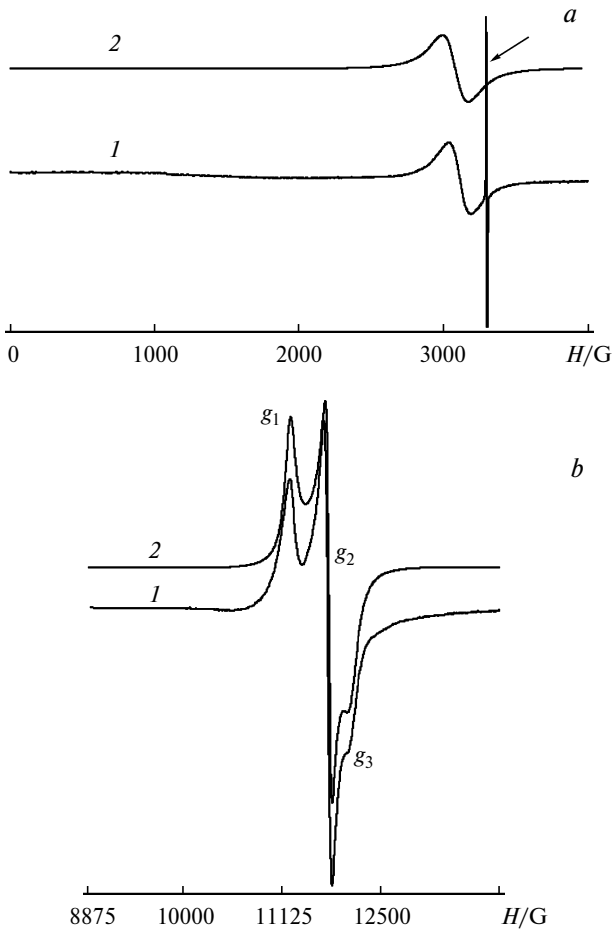

Fig. 1. Experimental ESR spectra (*1*) of a powder of $[\{Cu(NH_3)(threo\text{-tab})\}_2Fe(CN)_6]\cdot 8H_2O$ recorded at 300 K at a frequency of 9.5 (*a*) and 35.5 GHz (*b*) and the corresponding simulated ESR spectra (*2*); the signal of diphenylpicrylhydrazyl is indicated by an arrow.

The ESR spectrum of a powdered sample recorded at a frequency of 9.5 GHz (see Fig. 1, *a*) shows a single symmetrical line at $g = 2$ with a half-width $\Delta H = 90$ G. The central part of the line is described by the Lorentz function; the wings, by the Gaussian function. The central part of the line is narrowed due to an exchange interaction. At a frequency of 35.5 GHz, the ESR spectrum becomes resolved (see Fig. 1, *b*).

Results and Discussion

In the structure of $[\{Cu(NH_3)(\textit{threo}\text{-tab})\}_2Fe(CN)_6]\cdot 8H_2O$, the Cu atoms are linked to each other by the *threo*-tab molecules to form the infinite $[Cu(NH_3)(\textit{threo}\text{-tab})]_\infty$ chains, which, in turn, are linked by the *trans*-CN groups of the $[Fe(CN)_6]^{4-}$ anions to form polymeric layers (Fig. 2). The Cu atoms are coordinated by four N atoms of the amino groups of the *threo*-tab ligands to form square-planar CuN_4 fragments. The Cu—N(NH_2) distances in these fragments are in a range of 2.006(4)—2.025(4) Å. Each Cu atom is additionally coordinated by one N atom of the ammonia molecule (Cu—N(NH_3), 2.689(4) Å). This N atom is in the *trans* position with respect to the N atom of the CN group of the $[Fe(CN)_6]^{4-}$ anion. The Cu—N(CN) distances are 2.434(5) and 2.563(5) Å. Therefore, the coordination environment of the Cu atoms can be described as a distorted 4 + 1 + 1 octahedron. The water molecules of crystallization are located between the polymeric layers. The space group $P2_1$ unambiguously confirms the chirality of the resulting compound, which is a result of the chiral nature of the *threo*-tab ligand.

An analysis of the ESR spectra and their simulation using the WinEpr and Simfonia programs (Bruker) demonstrated that the complex structure of the spectra is associated with anisotropy of the *g* factor of the paramagnetic center with $S = 1/2$. This is confirmed by a good agreement between the experimental and simulated spectra calculated with the use of the above-mentioned programs. The calculated *g* factors are given in Table 2.

The *g* factors correspond to the *g* factor for distorted octahedral complexes of copper with the nearest nitrogen environment.[15] The complex under study is most structurally similar to the $Cu(H_2O)(NH_3)_5^{2+}$ complex characterized by the average *g* factor of 2.118.[16,17]

To determine the principal axes of the *g* tensor with respect to the crystal axes, we recorded the angular dependence of the single-crystal ESR spectrum (in two mutually perpendicular planes, *zx* and *xy*).

In the *xy* plane, the *g* factor weakly changes in the range from 2.056 to 2.103, which is evidence in favor of the plane of the g_1 and g_2 values of the *g* factor. This corresponds to the plane perpendicular to the *c* crystal axis. In the *zx* plane, the values of the *g* factor vary from 2.056 to 2.192, which is indicative of the plane passing through the *c* crystal axis (Fig. 3).

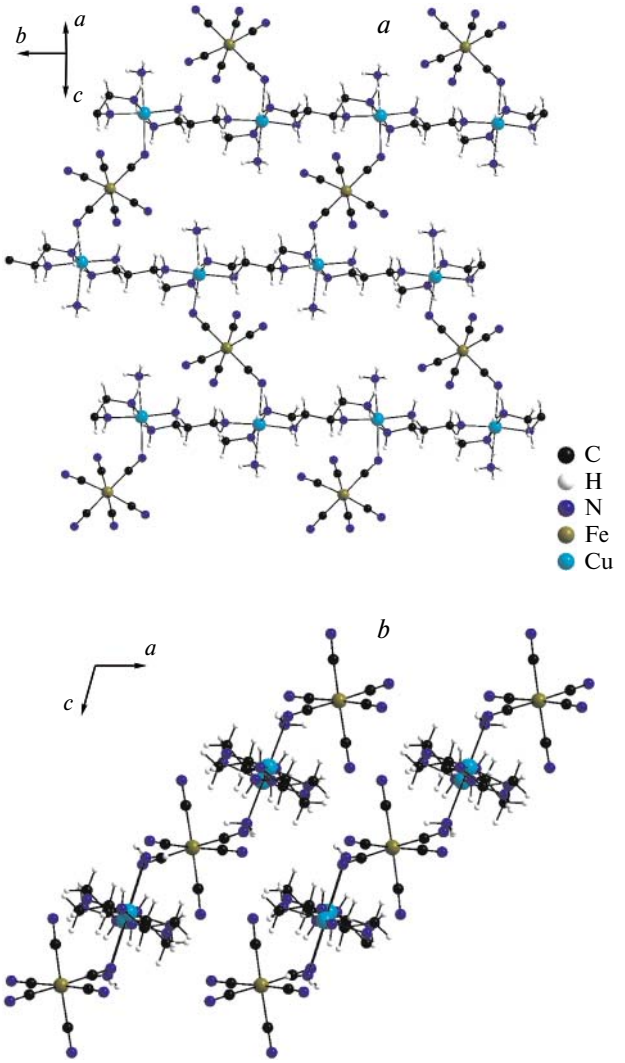

Fig. 2. Structure of the polymeric layer of $[\{Cu(NH_3)(\textit{threo}\text{-tab})\}_2Fe(CN)_6]$ (*a*) and the mutual arrangement of the layers in the structure of $Cu(NH_3)(\textit{threo}\text{-tab})\}_2Fe(CN)_6]\cdot 8H_2O$ (*b*). *Note.* Fig. 2 is available in full color in the on-line version of the journal (http://www.springerlink.com/issn/1573-9171/current) and on the web-site of the journal (http://russchembull.ru).

The maximum value of the *g* factor corresponds to the direction perpendicular to the plane of the N atoms of the CuN_4 fragment. The observed rhombic *g* factor can be attributed both to the difference in the Cu—N distances in the planar square and the averaging of the *g* factor in the case of exchange interactions between Cu^{2+} ions.

Table 2. The *g* factors for the ESR spectrum of the $[\{Cu(NH_3)(\textit{threo}\text{-tab})\}_2Fe(CN)_6]\cdot 8H_2O$ complex

Frequency/GHz	g_1	g_2	g_3
9.5	2.117	2.117	2.117
35.5	2.056	2.103	2.192

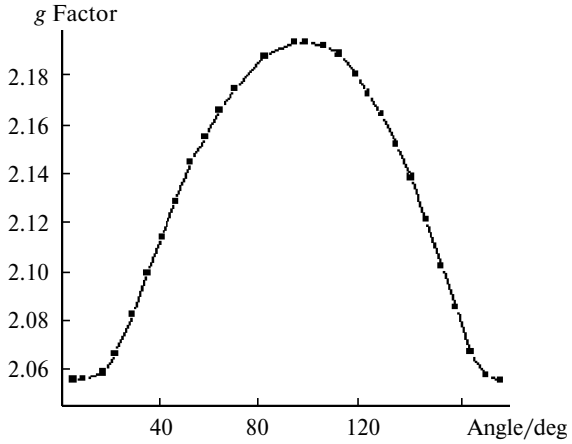

Fig. 3. Angular dependence of the single-crystal ESR spectrum of $[\{Cu(NH_3)(\textit{threo}\text{-tab})\}_2Fe(CN)_6]\cdot 8H_2O$ in the *zx* plane.

The parameters of the dipole-dipole interactions between the Cu^{2+} ions were calculated taking into account that the shortest distance between the Cu atoms in this polymer corresponds to the Cu—Fe—Cu bridge. For this purpose, the point dipole model and the X-ray diffraction data were used. The parameter *D* is 38 G, which is substantially smaller than the linewidth in the ESR spectrum. The absence of a hyperfine structure from the Cu atoms is due to exchange interactions between the Cu^{2+} ions in the polymeric structure.

To summarize, we synthesized the new polymeric complex $[\{Cu(NH_3)(\textit{threo}\text{-tab})\}_2Fe(CN)_6]\cdot 8H_2O$ by the reaction of $[Fe(CN))_6]^{4-}$ with copper(II) chloride and (2*S*,3*S*)-1,2,3,4-tetraaminobutane. This complex was structurally characterized. The reaction with the use of the starting bis-bidentate chiral *threo*-tab ligand gives rise to the chiral crystal structure of the compound, in which the infinite $[Cu(NH_3)(\textit{threo}\text{-tab})]_\infty$ chains are linked to each other by $Fe(CN)_6]^{4-}$ anions through *trans*-CN ligands to form polymeric layers. The ESR data demonstrate that the copper atoms in this compound are in the Cu^{2+} state and confirm the distorted octahedral coordination of the Cu atom and the presence of the N atoms in the nearest environment.

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Received January 12, 2007;
in revised form February 13, 2007